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Enhancing the properties of ceramic products through mixture design and response surface analysis

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Abstract

In products consisting of several components, the physical and engineering properties are a function of the proportions of the components. In this work, statistical combinations of a three-component mixture were designed to obtain synergetic values of mechanical strength of a cement mixture, constituted by lime, fly ash and water. The response surface method using a mixture design of a constrained triangular surface was applied to analyse the data obtained. The results were very satisfactory for characterizing and predicting the fracture strength of hardened specimens as a function of the composition. It is concluded that the use of this mathematical procedure can be an important tool to help to understand the behaviour of these types of ceramic products.

Keywords: Cements; Mechanical properties; Mixture design; Strength

1. Introduction

The design of experiments with mixtures and the applied response surface analysis has been mentioned in many investigations for obtaining product compositions or formulations with optimized properties. Many materials are formed by the mixture of several components, whose characteristics, such as the quality of the product being manufactured, depend on the relative proportions of the components in the mixture. The mixture design approach has been used, for example, in the optimization of formulations of food,[1] paint,[2] polymers,[3] asphalt,[4] concrete,[5] glass[6] and ceramic frits.[7] The synergetic effect of a combination of two or more components on a property of interest can be easily identified by means of a mixture design approach.

In a mixture experiment design, the total amount is held constant and a measured property of the mixture changes when the proportions of the components of the mixture are changed. Therefore, the main purpose of using this methodology is to verify how the properties of interest are affected by the variation of the proportions of the mixture components.

The determination of best compositions for a ceramic product can be accomplished by using composition–property triaxial diagrams. In addition, simplified polynomials, which define a so-called response surface, may correlate the property of interest to the proportions used. This makes the quantitative estimation of properties of any formulation in the studied system possible, without performing a large number of experiments. Response surfaces can be used to satisfy certain criteria, for instance, to maximize a property at the lowest cost and/or the robustness of a process, that is, to ensure that it is more insensitive to unexpected variations.

This study presents the synergetic effect of the composition of a cement mixture, constituted by lime, fly ash and water, on the fracture strength under compression of hardened specimens. These materials are characterized by a brittle mechanical behaviour with very little energy absorption, as typically for ceramic materials.

2. Experimental procedure

2.1. Mixture design and triaxial diagrams

Triaxial diagrams are a common mean to express compositions usually employed for obtaining certain

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ceramic products. It is a graphic representation of combinations of raw materials, rather than a predictive illustration of product phases as a function of primary phases and temperature, as it is the case for thermodynamic ternary diagrams, as known in materials science.

Frequently in order to form a valid mixture from which an acceptable product can be made, a component must be present above some minimum amount. The effect of limiting the components in a mixture is that the desired combinations are restricted to the subregion of a composition diagram. The so-called pseudocomponents, generated from the original components, are commonly used for modeling the surface over the subregion with a polynomial equation.

In the experimental design used here, the proportions of the original components varied from 7.9 to 38.9% for lime, 38.1 to 67.6% for fly ash and 15.1% to 40.5% for water. All compositions are expressed in mass per cent. The whole experiment was accomplished by two series of mixture designs. In the first approach 13 combinations were tested, and in the final approach nine combinations were performed to better identify the region of interest.

2.2. Raw materials and product

This research work is based on a three-component pozzolanic cement, constituted by lime, fly ash and water. Hydraulic or pozzolanic cements are pre-reacted compounds of calcium oxide and silica, alumina, and iron oxide that have been ground to a fine powder. When mixed with water, the compounds harden into a strong product, with relatively little change in volume. Reaction bonds and hydraulic cements are widely used as binders in construction materials and for refractories.

The raw materials used are either commercial products or industrial wastes. The main objective of the present research is to explain how the mixture design works, rather than exploring a ceramic product in particular. In this way, those materials were chosen because of their availability and easiness of processing:

- fly ash, originated from burning coal in a thermoelectrical power generation plant (Jorge Lacerda Plant, Capivari de Baixo, SC, Brazil);
- commercial lime (hydrated calcium oxide); and
- municipal tap water.

An average chemical composition of fly ash and lime is presented in Table 1. A typical SEM micrograph of pozzonalic product, obtained from a reaction between fly ash, lime and water, is shown in Fig. 1. The inner sphere is a fly ash particle partially reacted.

Table 1
Chemical composition of fly ash and lime, expressed in oxides

Composition (wt%)	Fly ash	Hydrated lime
SiO_2	53.60	0.3
Fe_2O_3	8.33	–
Al_2O_3	28.60	–
CaO	1.35	71.40
MgO	0.91	–
Na_2O	1.10	–
K_2O	2.32	–
SO_3	0.82	–
Lost on ignition	4.01	28.20
Insoluble matter	0.39	–

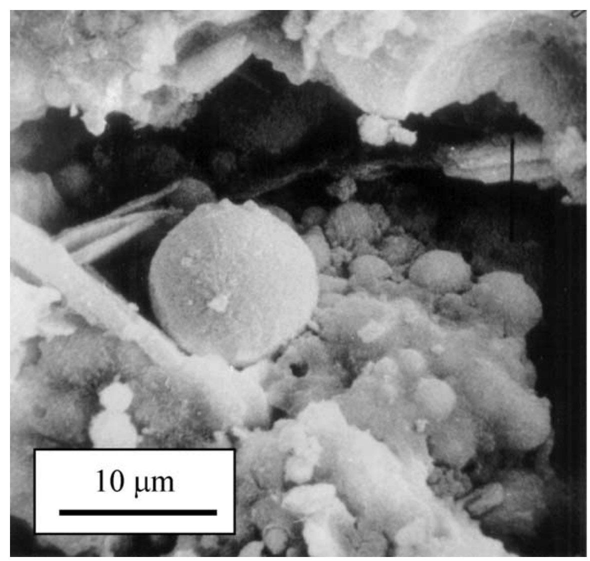

Fig. 1. Scanning electron micrograph of a pozzolanic product after hydration.

2.3. Sample preparation and measurements

Initially each dry cement composition was mixed manually, and then mechanically in a low speed mixer for 5 min. After adding the suitable amount of water for obtaining fixed moisture content, the mixture was homogenized for another 5 min.

The cement paste was poured into a die of a mechanical press. Cylindrical bodies of 10 cm diameter and 20 cm height were obtained under compaction pressures of 1.30 MPa (132,084 kg_f/m^2).

The specimens were brought in plastic bags to avoid the carbonation due to the carbon dioxide present in the air. The hydration reaction was set to 28 days. A standard procedure of simple compression test for brittle materials was then carried out. For each mixture composition, three specimens were submitted to mechanical tests, and the strength at fracture under compression was measured.

2.4. Regression model and response surface analysis

A complete mathematical and statistical theory on experimental designs of mixtures is available elsewhere.[8,9] For instance, a second-degree polynomial model to suit the experimental data can be defined according to the expression:

$$MR = b_1X + b_2Y + b_3Z + b_{12}XY + b_{13}XZ + b_{23}YZ \quad (1)$$

where MR is the expected modulus of rupture (fracture strength) under simple compression, X is the amount of lime in wt.%, Y is the amount of fly ash in wt.%, Z is the amount of water, in wt.%, and b_1, b_2, b_3, b_{12}, b_{13}, b_{23} are the coefficients of the adjusted equation.

This quadratic model can be used for obtaining the response surface to be analysed.

3. Results and discussion

The mixture design for the first approach suggested 13 experimental points, each corresponding to a mixture composition. In this case, the components are indeed pseudo-components (expressed here with an *); that is, water* is not pure water, but the richest composition in water of a restricted area inside the original diagram. In the same way, lime* and fly ash* are the richest compositions respectively in lime and fly ash. For each point an average modulus of rupture under compression was determined, Table 2. Standard deviations of measured values were within 10% in respect to the average value. These numerical results are represented in a triangular graph, Fig. 2, which shows the level curves of modulus of rupture as a function of the composition, obtained from a quadratic regression. The 13 experimental points are also represented in the graph. A high synergetic effect can be observed in the central area of this graph. It means that the combination of the three components leads to higher values of mechanical strength when compared to the single components. The highest values of modulus of rupture, above 3.12 MPa, are around point 9 (about 1/3 from each component).

In order to find a better definition of the region with higher MR values, a second experimental approach was performed around the central circular area. This time, a constrained area inside the previous experimental region was analysed. Another series of pseudocomponents were used, namely 7.9–29.1% for lime, 38.1–60.0% for fly ash and 15.1–40.5% for water.

Table 2
Mixtures used in the first experimental approach

Point	Lime (%)	Fly ash (%)	Water (%)	MR (MPa)
1	38.91	38.06	23.03	1.31
2	07.93	67.57	24.50	0.66
3	38.91	46.00	15.09	1.26
4	17.34	67.57	15.09	0.65
5	14.00	38.06	40.54	0.62
6	7.93	51.53	40.54	0.93
7	7.93	59.55	32.52	1.19
8	38.91	42.03	19.06	1.37
9	30.15	38.06	31.78	1.80
10	12.63	67.57	19.79	0.66
11	28.12	56.78	15.09	1.82
12	14.66	44.79	40.54	1.10
13	22.07	51.46	26.46	3.69

Table 3
Mixtures used in the second experimental approach

Point	Fly ash (%)	Lime (%)	Water (%)	MR (MPa)
1	30.15	38.06	31.78	1.80
2	14.66	44.79	40.54	1.10
3	28.12	56.78	15.09	1.82
4	07.93	59.55	32.52	1.19
5	22.41	41.42	36.16	2.12
6	29.14	47.42	23.43	3.54
7	18.02	58.16	23.80	2.97
8	11.29	52.17	36.53	1.92
9	20.21	49.79	29.98	3.50

Similarly, the experiment was performed in this case with 9 mixture points, shown in Table 3. In Fig. 3 the corresponding response surfaces are presented. In this case, the new pseudocomponents are expressed with an #. Essentially, the same behaviour in Fig. 2 can be observed. Another way to express the later results is to present a three-dimensional graph, Fig. 4. In both cases, the experimental points are also shown.

A second-degree polynomial model to suit these experimental data can be expressed as follows according to the original components:

$$MR = \text{-}60.30X - 31.55Y - 80.04Z + 154.59XY + 157.33XZ + 203.71YZ \quad (2)$$

The positive coefficients, corresponding to the interactions between XY (lime–ash), XZ (lime–water), and YZ (ash–water), represent the synergetic effect of the mixture of components on the expected value for mechanical strength under simple compression (MR). The values of 19.91 of lime, 51.02 of ash and 29.08% of water correspond, approximately, to the maximum of the function. In this case, the maximum value modulus of rupture should be expected around 3.65 MPa.

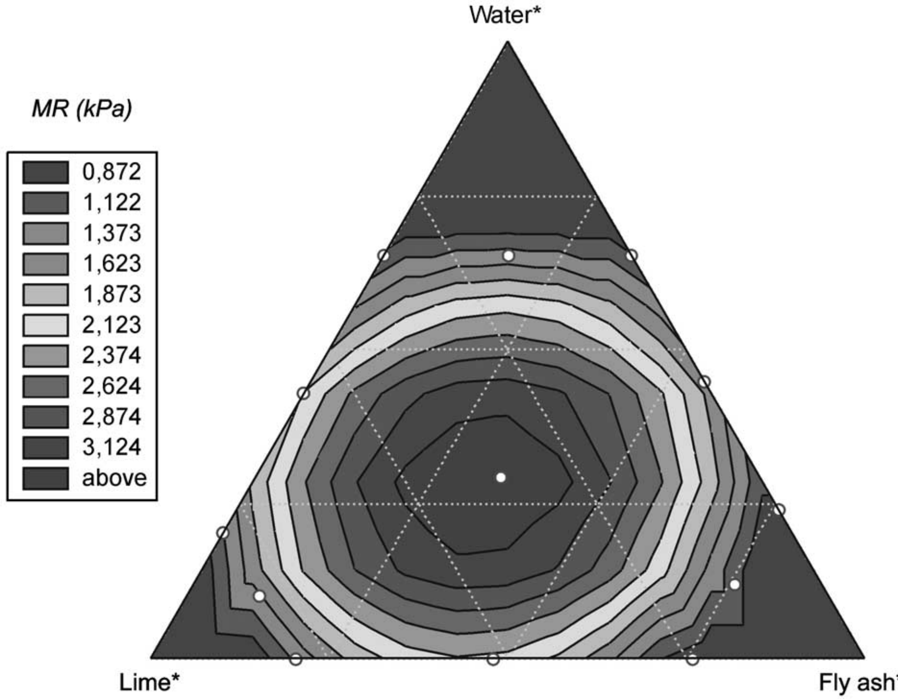

Fig. 2. Response surface of the expected compressive fracture strength for the first experimental approach as a function of pseudocomponents (*).

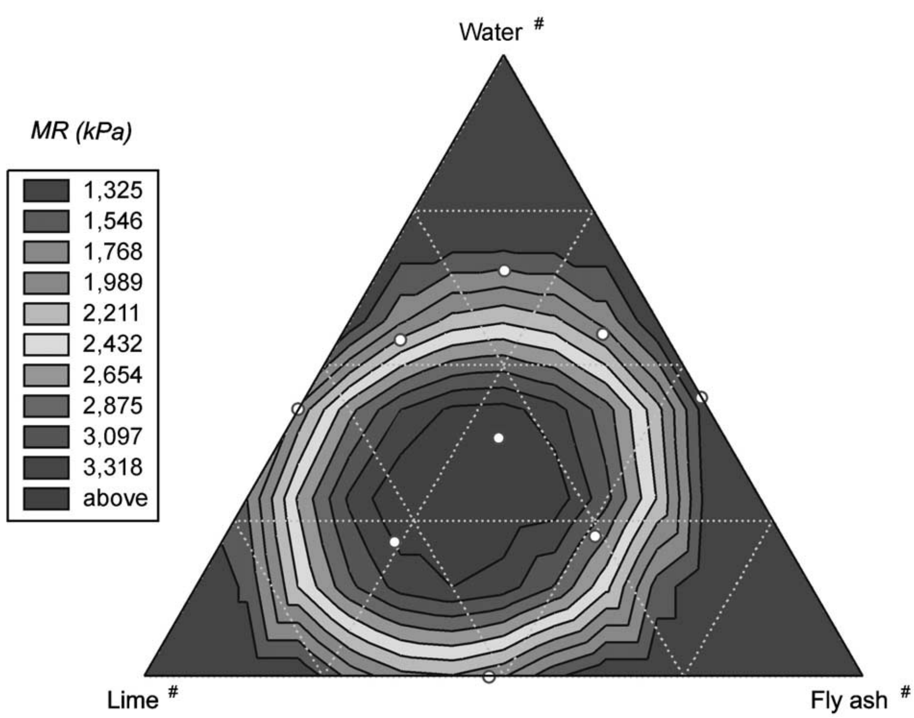

Fig. 3. Response surface of the expected compressive fracture strength for the second experimental approach as a function of pseudocomponents (#).

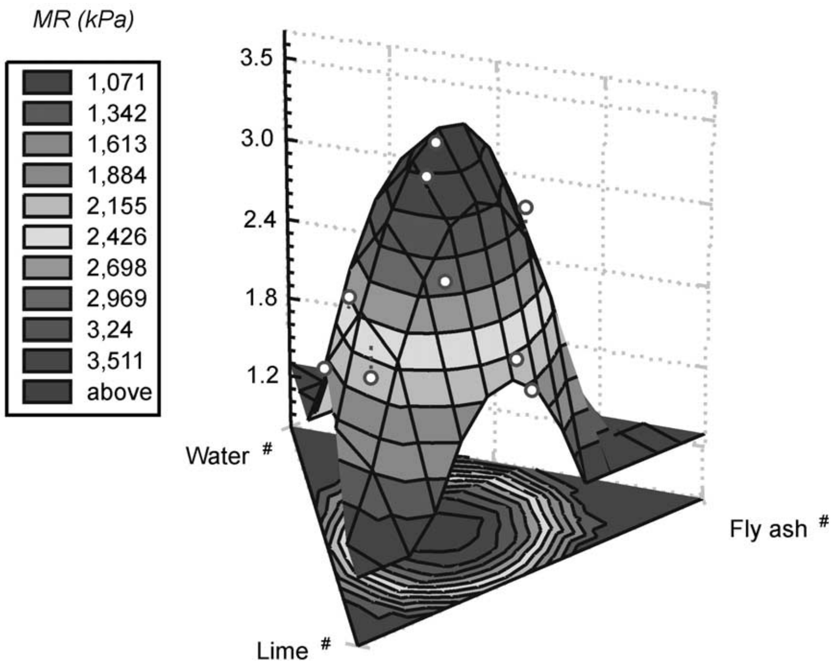

Fig. 4. Spatial graph of expected compressive fracture strength for the second experimental approach as a function of pseudocomponents.

4. Conclusions

- These studies have showed the possibility of using the mixture design and response surface method to characterize and predict synergetic effects of a component on a measured property.
- Particularly, the measured values of mechanical strength of hardened cement specimens depends strongly on the interaction of lime, fly ash and water.
- A suitable composition area, considering higher values of modulus of rupture, can be identified graphically or mathematically.
- A single composition corresponding to the maximum expected strength can be calculated from a quadratic regression equation.
- Eventually, other properties along with mechanical strength could be considered using the response surface analysis based on a experiment with mixtures.

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